

BEST AVAILABLE COPY

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 November 2003 (13.11.2003)

PCT

(10) International Publication Number
WO 03/093392 A1

(51) International Patent Classification⁷: C09K 7/06,
C10G 7/00

(74) Agents: DUNLOP, Alan, J., S. et al.; Hahn & Hahn Inc.,
Hahn Forum, 222 Richard Street, Hatfield, 0083 Pretoria
(ZA).

(21) International Application Number: PCT/ZA02/00086

(22) International Filing Date: 24 May 2002 (24.05.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2002/3429 30 April 2002 (30.04.2002) ZA

(81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for all designated States except US*): THE PETROLEUM OIL AND GAS CORPORATION OF SOUTH AFRICA (PTY)LTD [ZA/ZA]; Duinzicht Avenue, Mossel Bay, 6500 Cape (ZA).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): DUNLOP, Carl [ZA/ZA]; Duinzicht Avenue, Mossel Bay, 6500 Cape (ZA). HLOHLOZA, Stewart [ZA/ZA]; Duinzicht Avenue, Mossel Bay, 6500 Cape (ZA). HOFFMANN, Petrus, Johannes [ZA/ZA]; Duinzicht Avenue, Mossel Bay, 6500 Cape (ZA). KNOTTENBELT, Cyril, David [ZA/ZA]; Duinzicht Avenue, Mossel Bay, 6500 Cape (ZA). WALLISER, Leon [ZA/ZA]; Duinzicht Avenue, Mossel Bay, 6500 Cape (ZA).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/093392 A1

(54) Title: PROCESS FOR REDUCING THE TOXICITY OF HYDROCARBONS

(57) Abstract: A method for reducing the sediment toxicity of a composition, which includes a mixture of hydrocarbons, the mixture including hydrocarbons having a boiling point above about 270 °C and below about 340 °C, is provided. The method includes the steps of fractional distilling of the composition and collecting a fraction of hydrocarbons having a boiling point above about 270 °C and below about 340 °C. The sediment toxicity may be towards (*Leptocheirus plumulosus*) and the fraction of hydrocarbons may have a median lethal concentration (LC₅₀) of more than about 500 mg/kg and a Sediment Toxicity Ratio (STR) of greater than about 1.

Title: Process for Reducing the Toxicity of Hydrocarbons

5

Technical field of the invention

This invention relates to a method for reducing the toxicity of a mixture of hydrocarbons by means of fractional distillation, a distillate having a reduced toxicity and a composition including the distillate.

10

Background to the invention

Refined crude or synthetic oils or, compositions which include refined crude or synthetic oils, released into the environment are toxic and/ or detrimental to the environment and are often used in industry with negative effects to the environment, for example, drilling fluids (sometimes called muds) used in offshore oil and gas production and exploration. Drilling fluids are used to lubricate the drill bit and to carry the debris, such as drill cuttings, up to the surface for disposal. The debris is normally separated from the drilling fluids, however, the debris retain a layer of the drilling fluid. The oil covered debris resulting from such well boring operations need to be shipped to land for safe disposal or, if it were to be discharged onto the seabed or overboard into the sea, it needs to comply with strict environmental impact restrictions. Due to the high expense of shipping and disposing of the mud drilling compositions, a need exists to use drilling fluid which can be discharged onto the seabed or overboard and which complies with the strict environmental impact restrictions. One such requirement is the Environmental Protection Agency (EPA) LC₅₀ requirement of more than 30 000 result in a Mysid shrimp (*Mysidopsis Bahia*) bioassay prescribed in 1984 EPA-600/3-84-067. Generally, the Mysid shrimp bioassay measures the toxicity of the water column in which the shrimps live. Recently it became apparent that not only is the toxicity of the water column relevant, but even more so is the toxicity of the seabed sediment, onto which discharged debris

15

20

25

30

settle after it has been discharged overboard. Therefore, more relevant for drilling fluids used where the debris is to be discharged overboard, is the requirement that oils used for the manufacture of such drilling fluids pass a stringent ten day marine amphipod (*Leptocheirus plumulosus*) acute sediment toxicity test in accordance with American Society for Testing and Materials (ASTM) Guideline E 1367, EPA 600/R-94/025, which tests the toxicity of the actual marine sediment. This test is especially relevant to all offshore drilling platforms since the discharge of toxic drilling mud compositions from a drilling platform onto the seabed would have a significant negative environmental impact on the seabed.

In this specification, the hydrocarbons will be understood to be a collective term for molecules comprising carbon and hydrogen only and include non cyclic saturated hydrocarbons referred to as "paraffins", unsaturated hydrocarbons referred to as "olefins", cyclic hydrocarbons referred to as "cycloparaffins" and aromatic hydrocarbons referred to as "aromatics". Straight chain paraffins will be referred to as n-paraffins and branched paraffins referred to as iso-paraffins. Synthetic hydrocarbons will be understood to mean any hydrocarbons derived from a chemical process in which a chemical reaction takes place, as opposed to natural hydrocarbons, which is refined or distilled from crude oil.

Natural hydrocarbons, which are refined or distilled from crude oil are normally contaminated with high levels aromatics and are relatively toxic to marine life, making these drilling fluids that contain "natural" crude hydrocarbons environmentally unacceptable. High levels of n-paraffins in these fluids would have poor cold flow characteristics limiting their application in cold environments due to formation of waxy deposits.

The process for the preparation and use of plant or vegetable oil based environmentally friendly drilling fluid has been described in US patent No. 4,631,136.

The use of synthetic hydrocarbons became popular due to their low aromatic content and availability. Several patents described the use of synthetic hydrocarbons for drilling fluids. US patent No. 5,096,883 discloses the use of C₁₈ to C₄₀ hydrocarbons derived from dimerised 1-decene which is esterified. The good biodegradability of esters is well known, but esters are hydrolytically unstable. US patent No. 5,589,442 discloses the use of non alpha, linear internal C₁₄ to C₁₈ olefins obtained by an alpha olefin isomerisation process. US patent No. 5,569,642 discloses the use of a preferable C₁₄ to C₂₀ blend of n-paraffins and iso-paraffins. This patent also teaches that iso-paraffins having up to 40 carbon atoms per molecule are liquids over the temperature range of interest for drilling fluids, whereas, n-paraffins having more than about 16 to 23 carbon atoms per molecule are waxy solids. This is important with regard to the viscosity and rheology of drilling fluids. Similarly, US patent No. 5,866,748 discloses the use of a mixture of C₈ to C₂₀ n-paraffins and iso-paraffins derived from hydro isomerisation of C₈ to C₂₀ n-paraffins. US patent No. 6,096,690 discloses, by way of example, the use of a mixture of C₁₃ to C₁₈ n-paraffins and iso-paraffins derived from hydro cracking of Fisher Tropsch waxes. This patent further claims that mono methyl iso-paraffins are less toxic than more branched iso-paraffins. US patent No. 5,498,596 discloses the use of a mixture of C₁₀ to C₁₈ paraffins from mineral oils and poly(alpha olefins) derived from the dimer of decene. US patent No. 5,189,012 and a related US Registered Statutory Invention No. H1000 discloses the use of branched chain oligomers and unhydrogenated synthetic hydrocarbon compositions of C₉ to C₇₁ synthesized from oligomerization of C₂ to C₁₄ olefins. US patent No. 5,635,457 discloses, in one embodiment, the use of a hydrocarbon mixture of which at least 95% has 11 or more carbon atoms and, in another embodiment, at least 95% has 10 or more carbon atoms.

Each of the above patents utilised a water column toxicity bioassay. All, except US 5,498,596 which used a marine Copepod bioassay, used the Mysid shrimp bioassay.

The applicant has found that, for the (*Leptocheirus plumulosus*) acute sediment toxicity test, the toxicity rapidly decreases for a distillation fraction of hydrocarbons the higher its boiling point above about 270°C. A trend in toxicity reduction was noted for toxicity as the boiling range of the fluid
5 increased.

General description of the invention

According to a first aspect of the invention there is provided a method
10 for reducing the sediment toxicity of a composition which includes a mixture of hydrocarbons, the mixture including hydrocarbons having a boiling point above about 270°C and below about 340°C, the method including the steps of:

- fractional distilling of the composition; and
- 15 collecting a fraction of hydrocarbons having a boiling point above about 270°C and below about 340°C.

It will be appreciated that the average molecular weight of the hydrocarbons of such collected fractions will depend on its isomeric content.
20 In general, the more branched the hydrocarbons the higher its average molecular weight for a certain boiling point.

The sediment toxicity may be towards (*Leptocheirus plumulosus*) and the fraction of hydrocarbons may have a median lethal concentration (LC₅₀),
25 in accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than about 500 mg/kg and a Sediment Toxicity Ratio (STR) of greater than about 1.

The mixture of hydrocarbons may include hydrocarbons having a boiling point above about 280°C and a fraction of hydrocarbons having a
30 boiling point above about 280°C, a median lethal concentration (LC₅₀), in accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than about 2000 mg/kg and a STR of about 1 or less, may be collected.

The mixture of hydrocarbons may include hydrocarbons having a boiling point above about 290°C and a fraction of hydrocarbons having a boiling point above about 290°C, a median lethal concentration (LC₅₀), in accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than
5 about 2000 mg/kg and a STR of about 1 or less, may be collected.

The mixture of hydrocarbons may include hydrocarbons having a boiling point above about 300°C and a fraction of hydrocarbons having a boiling point above about 300°C, a median lethal concentration (LC₅₀), in
10 accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than about 2000 mg/kg and a STR of about 1 or less, may be collected.

The mixture of hydrocarbons may include hydrocarbons having a boiling point above about 310°C and a fraction of hydrocarbons having a boiling point above about 310°C, a median lethal concentration (LC₅₀), in
15 accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than about 2000 mg/kg and a STR of about 1 or less, may be collected.

The mixture of hydrocarbons may include hydrocarbons having a boiling point above about 320°C and a fraction of hydrocarbons having a boiling point above about 320°C, a median lethal concentration (LC₅₀), in
20 accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than about 15000 mg/kg and a STR of about 1 or less, may be collected.

25 The composition may include isoparaffins and/ or n-paraffins.

The composition may include aromatic hydrocarbons of up to about 0.1% maximum, preferably none.

30 The toxicity of the composition may be reduced for use in base oils and drilling fluids, or drilling mud compositions useful in the exploration for, and/ or production of oil and gas.

The composition may be natural hydrocarbons selected from low aromatic crude derived diesels, mineral oils, hydrocarbons and/ or n-paraffins derived from molecular sieving or extractive distillation processes.

- 5 The composition may also be synthetic hydrocarbons selected from a distillate product of an oligomerization of olefins process such as a Conversion of Olefins to Diesel (COD) process (SA Patent 92/0642), or other dimerised or trimerised olefins, which could be further hydrogenated if required. A zeolite type catalyst may catalyse such a conversion of olefins.
- 10 Also, the composition may be iso-paraffins derived from skeletal isomerisation processes, and hydrocarbons derived from high or low temperature Fisher-Tropsch processes.

- 15 According to a second aspect of the invention, there is provided a method for producing a base oil for use in manufacturing of a drilling fluid, the method including the method for reducing the sediment toxicity of a composition as described above.

20

- According to a third aspect of the invention, there is provided a method of manufacturing a drilling fluid, the method including the step of mixing the fraction of hydrocarbons, as described above, with one or more of diluents, synthetic or natural esters, plant oils, thinning agents, viscosifiers, emulsifiers,
- 25 wetting agents, weighting agents, proppants, fluid loss control agents and/ or particulate matter.

- According to a fourth aspect of the invention, there is provided the use
- 30 of a fraction of hydrocarbons, collected from a method as described above, for the manufacture of a base oil and/ or a drilling fluid, or a drilling mud composition useful in the exploration for, and production of oil and gas.

According to a fifth aspect of the invention, there is provided a fraction of hydrocarbons, collected from a method as described above, for the manufacture of a base oil and/ or a drilling fluid, or a drilling mud composition useful in the exploration for, and production of oil and gas.

5

The fraction may be a mixture of predominantly iso-paraffins and may have an initial boiling point as tested by ASTM D 86 of about 250°C, preferably at least about 260°C and more preferably at least about 270°C and even more preferably at least about 280°C. The fraction may have a final
10 boiling point as tested by ASTM D 86 of between about 300°C and 340°C, preferably about 330°C. The flash point of the fraction as tested by ASTM D 93 may be at least about 95°C, more typically above about 120°C and most typically about 130°C. The viscosity of the fraction at 40°C as measured by
15 ASTM D 445 may fall between about 2 cSt and 5 cSt. The dynamic viscosity of the fraction at 0°C, as tested by the Brookfield Viscometer equipped with a UL adapter may be less than 20 cP, more typically less than 15 cP. Fractions with a Brookfield Viscosity of less than 10 cP at 0°C, 60 rpm may also be typical. The pour point of the fraction may typically be lower than -55°C, more commonly lower than -50°C and most commonly lower than -40°C.
20 The naphthene content of the fraction may be greater than 5% m/m as measured by 12 x 12 Mass Spectrometry (MS) analyses. The portion boiling above C₁₅ may contain a minimum of 60% iso-paraffinic molecules, more preferably more than 70% iso-paraffin's and most preferably more than 80% iso-paraffins. The average molecular mass of the detoxified fluid would be
25 greater that 230.

The fraction may be a mixture of predominantly n-paraffins and may have an initial boiling point as tested by ASTM D 86 of about 250°C, preferably at least about 260°C, more preferably at least about 270°C and
30 even more preferably at least about 280°C. The fluid may have a final boiling point as tested by ASTM D 86 of between about 300°C and 340°C, preferably about 330°C. The flash point of this material as tested by ASTM D 93 may be at least about 95°C, more typically above about 120°C and most typically above about 130°C. The viscosity of the fluid at 40°C as measured by ASTM

D 445 may fall between about 2 cSt and 5 cSt. The pour point of this fluid may typically be lower than about 20°C. It will be appreciated that blends of this fraction with hydrocarbon mixtures having a lower pour point may be required to obtain a more suitable pour point, or solvents may be used where
5 needed. The naphthene content of the well fluid may be greater than 5% m/m as measured by 12 x 12 MS analyses. The portion boiling above C15 may contain a minimum of 60% n-paraffinic molecules, more preferably more than 70% n-paraffin's and most preferably more than 80% n-paraffins. The average molecular mass of the detoxified fluid would be greater than 230.

10

According to a sixth aspect of the invention, there is provided a base oil and/ or a drilling fluid, or a drilling mud composition useful in the exploration for, and production of oil and gas, the base oil and/ or a drilling fluid, or
15 drilling mud composition including a fraction of hydrocarbons collected from a method as described above.

The drilling fluid may include a fraction of hydrocarbons collected from a method described above, a C₁₂ – C₂₀ n-paraffin iso-paraffin mixture and a
20 C₂₃ ester. The C₁₂ – C₂₀ n-paraffin mixture may be a commercially available mixture and could be up to about 30% volume of the drilling fluid and the ester may be up to about 10% volume of the drilling fluid.

The drilling fluid may include up to about 70% of the predominantly iso-
25 paraffinic fraction described above and a portion containing up to about 30% C₁₁ to C₂₀ of n-paraffin's and not more than about 9.5% of a plant ester component. The C₁₁ to C₂₀ of n-paraffin's may be commercially obtained and may typically be derived from a Fisher-Tropsch process. The drilling fluid may have an initial boiling point as tested by ASTM D 86 of between about 210°C and 250°C, preferably about 240°C. The drilling fluid has a final boiling point
30 as tested by ASTM D 86 of about 300°C, preferably at least about 310°C, more preferably at least about 320°C and even more preferably about 330°C. Fluids boiling above 340°C may also be possible. The flash point of the drilling fluid as tested by ASTM D 93 is at least about 90°C, more typically

above about 100°C and most typically about 110°C. The viscosity of the fluid at 40°C as measured by ASTM D 445 may fall between about 2 cSt and 5 cSt. The dynamic viscosity at 0°C, as tested by the Brookfield Viscometer equipped with a UL adapter may be less than about 20 cP, more typically less than about 10 cP, even more typically less than about 9 cP and most typically less than about 8 cP. The pour point of the drilling fluid is typically higher than about -20°C, more commonly higher than about -15°C and most commonly higher than about -10°C. The naphthene content of the drilling fluid may be more than 5% m/m as measured by 12 x 12 MS analyses.

10

The portion of the drilling fluid boiling below C₁₅ may include a minimum of n-paraffin content of at least about 50%, more preferably more than about 60% n-paraffin's and even more preferably more than about 70% n-paraffin's. The portion of the drilling fluid boiling above C₁₅ may include a minimum of about 50% iso-paraffins, preferably more than about 60% iso-paraffins and more preferably more than about 70% iso-paraffins. The portion of the drilling fluid boiling above C₁₅ may contain a minimum of 2 %-oxygenated molecules. The average molecular mass of the detoxified fluid would be greater than 230.

20

Detailed description of the invention

The invention is now described in more detail and by way of non limiting examples.

25

In order for a drilling fluid to pass the stringent ten day marine amphipod (*Leptocheirus plumulosus*) acute sediment toxicity test in accordance with ASTM Guideline E 1367, EPA 600/R-94/025, a sample must exhibit a sediment toxicity ratio (STR) of less than or equal to 1.00 in order to pass the test. The STR was calculated using the following equation:

30

$$\frac{\text{LC}_{50} \text{ of Reference Material}}{\text{LC}_{50} \text{ of NAF} + (0.20 \times \text{LC}_{50} \text{ of Reference Material})}$$

where LC_{50} = median lethal concentration,

Reference Material = C_{16} - C_{18} internal olefin, and

NAF = non-aqueous fluid.

- 5 The LC_{50} value for different samples may vary from one batch to the other of marine organisms tested, *Leptocheirus* in this case, and an internal standard has therefore been built in i.e. the C_{16} - C_{18} Internal Olefin.

- 10 Table 1 shows a typical sediment toxicity profile of fractions of a zero aromatic containing hydrocarbon mixture derived from a conversion of olefins to diesel process.

15 Table 1

Fraction	Toxicity as LC_{50} mg/kg	STR	Ave Molecular Weight
Full boiling range	<1000	2.84	221
Boiling range 200 – 210°C	120	4.34	162
Boiling range 210 – 220°C	117	4.35	169
Boiling range 220 – 240°C	117	4.35	177
Boiling range 240 – 260°C	131	4.29	196
Boiling range 260 – 280°C	272	3.78	211
Boiling range 280 – 320°C	2147	1.41	237
Boiling range above 320°C	18227	0.22	298

Table 2 shows a typical sediment toxicity profile of fractions of a low aromatic content hydrocarbon mixture derived from a conversion of olefins to diesel process.

20

Table 2

Fraction	Toxicity as LC_{50} mg/kg	STR	Ave Molecular Weight
Full boiling range	<1000	>2	220
Boiling range 220 – 240°C	117	4.35	180
Boiling range 240 – 260°C	131	4.29	198
Boiling range 260 – 280°C	290	3.92	212
Boiling range 280 – 320°C	1784	1.61	238
Boiling range above 320°C	19314	0.21	297

Table 3 shows a typical sediment toxicity profile of fractions of a synthetic mixture of n-paraffins.

5

Table 3

Fraction	Toxicity as LC ₅₀ mg/kg	STR	Ave Molecular Weight
Full boiling range	<1000	<2	200
Boiling range 220 – 240°C	<1000	>1.6	166
Boiling range 240 – 260°C	<1000	>1.6	171
Boiling range 260 – 280°C	1299	1.33	183
Boiling range 280 – 320°C	4064	0.52	208

Tables 1 to 3 clearly show a tendency of lower sediment toxicity for higher boiling hydrocarbons with a sharp decline in toxicity at about a boiling point of above about 270°C.

10

Table 4 gives the characterisation of an example of a typical fraction of predominantly iso-paraffins collected by means of the method for reducing the sediment toxicity of a composition which include a mixture of hydrocarbons, in accordance with the invention.

15

Table 4

Properties	Units	Test method	Result
Sediment Toxicity Ratio		ASTM E 1367	<1.0
Sediment Toxicity	mg/kg	ASTM E 1367	>8000
Carbon Content	% Carbon	ASTM D 5291	85.16
Density @ 20°C	Kg/L	ASTM D 4052	0.8084
Flash point (PMcc)	°C	ASTM D 93	132.5
Aromatic content	% m/m	UOP 495	0.06
Total Sulphur	ppm m/m	ASTM D 3120	< 0.30
Kinematic viscosity @ 40°C	cSt	ASTM D 445	4.565
Kinematic viscosity @ 100°C	cSt	ASTM D 445	1.510
Refractive Index		ASTM D 1218	1.44726
Pour point	°C	ASTM D 97	<-51
Distillation		ASTM D 86	
- Initial boiling point	°C		275
- Final boiling point	°C		317
Average Molecular Mass			235

Table 5 gives the characterisation of an example of a typical fraction of predominantly n-paraffins collected by means of the method for reducing the sediment toxicity of a composition which include a mixture of hydrocarbons, in accordance with the invention.

5

Table 5

Properties	Units	Test method	Result
Sediment Toxicity Ratio		ASTM E 1367	<1.0
Sediment Toxicity	mg/kg	ASTM E 1367	>3000
Carbon Content	% Carbon	ASTM D 5291	84.74
Density @ 20°C	Kg/L	ASTM D 4052	0.7759
Flash point (PMcc)	°C	ASTM D 93	136.5
Aromatic content	% m/m	UOP 495	< 0.01
Total Sulphur	Ppm m/m	ASTM D 3120	< 0.10
Kinematic viscosity @ 40°C	cSt	ASTM D 445	3.168
Refractive Index		ASTM D 1218	1.43583
Pour point	°C	ASTM D 97	15
Distillation		ASTM D 86	
- Initial boiling point	°C		276
- Final boiling point	°C		310
Average Molecular Mass			232

Table 6 gives the characterisation of an example of a typical drilling fluid, in accordance with the invention.

10

Table 6

Properties	Units	Test method	Result
Sediment Toxicity Ratio		ASTM E 1367	<1.0
Sediment Toxicity	mg/kg	ASTM E 1367	>4000
Carbon Content	% Carbon	ASTM D 5291	84.44
Density @ 20°C	Kg/L	ASTM D 4052	0.8980
Flash point (PMcc)	°C	ASTM D 93	110
Aromatic content	% m/m	UOP 495	0.06
Total Sulphur	ppm m/m	ASTM D 3120	< 0.30
Kinematic viscosity @ 40°C	cSt	ASTM D 445	3.470
Dynamic viscosity @ 0°C	cSt	Brookfield	8.60
Pour point	°C	ASTM D 97	-19
Distillation		ASTM D 86	
- Initial boiling point	°C		244
- Final boiling point	°C		329
Average Molecular Mass			229

The applicant believes that the invention provides a flexible method for detoxifying hydrocarbons, which may be used in a variety of environmentally exposed applications. The invention also allows the rheology and other
5 characteristics of such detoxified fractions, as described, to be manipulated for use in specific applications.

CLAIMS:

1. A method for reducing the sediment toxicity of a composition which includes a mixture of hydrocarbons, the mixture including hydrocarbons
5 having a boiling point above about 270°C and below about 340°C, the method including the steps of:
fractional distilling of the composition; and
collecting a fraction of hydrocarbons having a boiling point above about 270°C and below about 340°C.
10
2. A method as claimed in claim 1, in which the sediment toxicity is towards *Leptocheirus plumulosus* and the fraction of hydrocarbons have a median lethal concentration (LC₅₀), in accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than about 500 mg/kg.
15
3. A method as claimed in claim 2, in which the mixture of hydrocarbons includes hydrocarbons having a boiling point above about 280°C and in which a fraction of hydrocarbons having a boiling point above about 280°C, a LC₅₀, in accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than
20 about 2000 mg/kg and a Sediment Toxicity Ratio (STR) of about 1 or less, is collected.
4. A method as claimed in claim 2 or claim 3, in which the mixture of hydrocarbons includes hydrocarbons having a boiling point above about
25 290°C and in which a fraction of hydrocarbons having a boiling point above about 290°C, a LC₅₀, in accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than about 2000 mg/kg and a STR of about 1 or less, is collected.
- 30 5. A method as claimed in any one of claims 2 to 4, in which the mixture of hydrocarbons includes hydrocarbons having a boiling point above about 300°C and in which a fraction of hydrocarbons having a boiling point above about 300°C, a LC₅₀, in accordance with ASTM Guideline E 1367, EPA

600/R-94/025, of more than about 2000 mg/kg and a STR of about 1 or less, is collected.

5 6. A method as claimed in any one of claims 2 to 5, in which the mixture of hydrocarbons includes hydrocarbons having a boiling point above about 310°C and in which a fraction of hydrocarbons having a boiling point above about 310°C, a LC₅₀, in accordance with ASTM Guideline E 1367, EPA 600/R-94/025, of more than about 2000 mg/kg and a STR of about 1 or less, is collected.

10

7. A method as claimed in one of claims 2 to 6, in which the mixture of hydrocarbons includes hydrocarbons having a boiling point above about 320°C and in which a fraction of hydrocarbons having a boiling point above about 320°C, a LC₅₀, in accordance with ASTM Guideline E 1367, EPA
15 600/R-94/025, of more than about 15000 mg/kg and a STR of about 1 or less, is collected.

20

8. A method as claimed in any one of the above claims, in which the composition includes isoparaffins and/ or n-paraffins.

9. A method as claimed in any one of the above claims, in which the composition includes less than 0.2% aromatic hydrocarbons.

10. A method as claimed in any one of the above claims, in which the
25 toxicity of the composition is reduced for use in base oils, drilling fluids, or drilling mud compositions useful in the exploration for, and/or production of oil and gas.

11. A method as claimed in any one of the above claims, in which the
30 composition includes natural hydrocarbons selected from low aromatic crude derived diesels, mineral oils, hydrocarbons and/ or n-paraffins derived from molecular sieving or extractive distillation processes.

12. A method as claimed in any one of the above claims, in which the composition includes synthetic hydrocarbons selected from a distillate product of a dimerization, trimerization or oligomerization of olefins process.
- 5 13. A method as claimed in claim 12, in which the synthetic hydrocarbons are olefins of a dimerization, trimerization or oligomerization process, which have been hydrogenated.
- 10 14. A method as claimed in claim 12 or claim 13, in which the olefins are oligomerised, dimerised or trimerised by means of a zeolite type catalyst.
- 15 15. A method as claimed in any one of claims 1 to 10, in which the composition includes iso-paraffins derived from skeletal isomerisation processes, or hydrocarbons derived from high or low temperature Fisher-Tropsch processes.
- 20 16. A method for producing a base oil for use in the manufacture of a drilling fluid, the method including the method for reducing the sediment toxicity of a composition as claimed in one of the above claims.
- 25 17. A method of manufacturing a drilling fluid, the method including the step of mixing a fraction of hydrocarbons collected from the method as claimed in any one of claims 1 to 15, with one or more of diluents, synthetic or natural esters, plant oils, thinning agents, viscosifiers, emulsifiers, wetting agents, weighting agents, proppants, fluid loss control agents and/ or particulate matter.
- 30 18. Use of a fraction of hydrocarbons, collected from a method as claimed in any one of claims 1 to 15, for the manufacture of a base oil and/ or a drilling fluid, or a drilling mud composition useful in the exploration for, and/or production of oil and gas.
19. A fraction of hydrocarbons, collected from a method as claimed in any one of claims 1 to 15.

20. A fraction of hydrocarbons as claimed in claim 19 for use in the manufacture of a base oil and/ or a drilling fluid, or a drilling mud composition useful in the exploration for, and/or production of oil and gas.

5

21. A fraction of hydrocarbons as claimed in claim 19 or claim 20, in which the fraction includes a mixture of predominantly iso-paraffins and the fraction having an initial boiling point of at least between about 250°C and about 280°C, a final boiling point of between about 300°C and 340°C, a flash point
10 of at least between about 95°C and 130°C, a viscosity at 40°C of between about 2 cSt and 5 cSt, a dynamic viscosity of the fraction at 0°C of less than 20 cP, and a pour point of lower than between -55°C and -40°C.

22. A fraction of hydrocarbons as claimed in claim 21, which has an initial
15 boiling point of at least about 280°C.

23. A fraction of hydrocarbons as claimed in claim 21 or claim 22, which has a final boiling point of about 330°C.

20 24. A fraction of hydrocarbons as claimed in any one of claims 21 to 23, which has a flash point of above about 95°C.

25. A fraction of hydrocarbons as claimed in claim 24, which has a flash point of above about 120°C.

25

26. A fraction of hydrocarbons as claimed in claim 25, which has a flash point of above about 130°C.

27. A fraction of hydrocarbons as claimed in any one of claims 21 to 26,
30 which has a dynamic viscosity of the fraction at 0°C of less than 15 cP.

28. A fraction of hydrocarbons as claimed in any one of claims 19 to 27, in which has the fraction includes naphthenes of more than 5% m/m.

29. A fraction of hydrocarbons as claimed in any one of claims 19 to 28, in which a portion boiling above the boiling point of C₁₅ hydrocarbons contains a minimum of 60% iso-paraffinic molecules.
- 5 30. A fraction of hydrocarbons as claimed in claim 29, in which a portion boiling above the boiling point of C₁₅ hydrocarbons contains more than 70% iso-paraffin's.
- 10 31. A fraction of hydrocarbons as claimed in claim 30, in which a portion boiling above the boiling point of C₁₅ hydrocarbons contains more than 80% iso-paraffins.
- 15 32. A fraction of hydrocarbons as claimed in any one of claims 19 to 31, in which the average molecular mass of the fraction is greater than 230.
- 20 33. A fraction of hydrocarbons as claimed in claim 19 or claim 20, in which the fraction includes a mixture of predominantly n-paraffins and the fraction having an initial boiling point of at least between about 250°C and 280°C, a final boiling point of between about 300°C and 340°C, a flash point of at least about 95°C, a viscosity at 40°C of between about 2 cSt and 5 cSt, and a pour point of lower than about 20°C.
- 25 34. A fraction of hydrocarbons as claimed in claim 33, which has an initial boiling point of at least about 280°C.
- 30 35. A fraction of hydrocarbons as claimed in claim 33 or claim 34, which has a final boiling point of about 330°C.
36. A fraction of hydrocarbons as claimed in any one of claims 33 to 35, which has a flash point of above about 120°C.
37. A fraction of hydrocarbons as claimed in claim 36, which has a flash point of above about 130°C.

38. A fraction of hydrocarbons as claimed in any one of claims 33 to 37, in which the average molecular mass of the fraction is greater than 230.

5 39. A drilling fluid useful in the exploration for and production of oil and gas, the drilling fluid including a fraction of hydrocarbons collected from a method as claimed in any one of claims 1 to 15.

40. A drilling fluid as claimed in claim 39, which includes a mixture of C₁₂ –
10 C₂₀ n-paraffins, C₁₂ – C₂₀ iso-paraffins and an ester.

41. A drilling fluid as claimed in claim 40, which includes a C₂₃ ester.

42. A drilling fluid as claimed in claims 40 or claim 41, in which the C₁₂ –
15 C₂₀ n-paraffin mixture includes a commercially available mixture and the C₁₂ – C₂₀ n-paraffin mixture making up, up to about 30% volume of the drilling fluid.

43. A drilling fluid as claimed in claim 42, in which the ester makes up, up to about 10% volume of the drilling fluid.

20

44. A drilling fluid as claimed in any one of claims 41 to 43, in which the iso-paraffins of the mixture are derived from a fraction as claimed in any one of claims 19 to 32 and makes up, up to about 70% of the drilling fluid and the n-paraffins make up, up to about 30% of the drilling fluid and the plant ester
25 component up to about 9.5% of the drilling fluid.

45. A drilling fluid as claimed in any one of claims 40 to 44, in which the C₁₁ to C₂₀ of n-paraffin's is commercially available and derived from a Fisher-Tropsch process.

30

46. A drilling fluid as claimed in any one of claims 39 to 45, which has an initial boiling point of between about 210°C and 250°C.

47. A drilling fluid as claimed in claim 46, which has an initial boiling point of about 240°C.
48. A drilling fluid as claimed in any one of claims 39 to 45, which has a
5 final boiling point of higher than between about 300°C and 320°C.
49. A drilling fluid as claimed in claim 48, which has a final boiling point of higher than about 330°C.
- 10 50. A drilling fluid as claimed in any one of claims 39 to 45, which has a flash point of at least between about 90°C and 100°C.
51. A drilling fluid as claimed in claim 50, which has a flash point of at least about 110°C.
- 15 52. A drilling fluid as claimed in any one of claims 39 to 51, which has a viscosity at 40°C of between about 2 cSt and 5 cSt or a dynamic viscosity at 0°C, of less than between about 20 cP and 9 cP.
- 20 53. A drilling fluid as claimed in claim 52, which has, where selected, a dynamic viscosity at 0°C, at 60 rpm of at least 8 cP.
54. A drilling fluid as claimed in any one of claims 39 to 53, which has a pour point higher than between about -20°C and -10°C.
- 25 55. A drilling fluid as claimed in any one of claims 39 to 54, which includes naphthenes of more than 5% m/m.
- 30 56. A drilling fluid as claimed in any one of claims 39 to 55, in which a portion of the drilling fluid boils below the boiling point of C₁₅, the portion including a minimum of between 50% and 70% n-paraffins.

57. A drilling fluid as claimed in any one of claims 39 to 56, in which a portion of the drilling fluid boils above the boiling point of C₁₅, the portion including a minimum of between about 50% and 70% iso-paraffins.

5 58. A drilling fluid as claimed in claim 57, in which the portion of the drilling fluid boiling above the boiling point of C₁₅ contains a minimum of 2 % oxygenated molecules.

59. A drilling fluid as claimed in any one of the claims 39 to 58, in which the
10 average molecular mass of the drilling fluid is greater than 230.

60. A drilling fluid as claimed in any one of claims 39 to 59, which includes one or more of diluents, synthetic or natural esters, plant oils, thinning agents, viscosifiers, emulsifiers, wetting agents, weighting agents, proppants, fluid
15 loss control agents and/ or particulate matter.

61. A method for reducing the sediment toxicity of a composition substantially as described herein

20 62. A method for producing a base oil substantially as described herein.

63. A method of manufacturing a drilling fluid substantially as described herein.

64. Use of a fraction of hydrocarbons substantially as described herein.

25

65. A fraction of hydrocarbons substantially as described herein.

66. A drilling fluid substantially as described herein.

30

INTERNATIONAL SEARCH REPORT

International Application No

PCT/02/00086

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09K7/06 C10G7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 096 690 A (MART CHARLES JOHN ET AL) 1 August 2000 (2000-08-01)	1-10, 15-27, 29-35, 38-54, 56-60
Y	column 2, line 64 - column 3, line 27 column 4, line 53 - line 58; claims 1,4,6; tables 2,3	1,11-14
X	GB 2 117 429 A (MILCHEM INC) 12 October 1983 (1983-10-12)	17-20, 28,32, 39, 46-55, 59,60
Y	page 1, line 60 - line 64 page 2, line 54 - page 3, line 16 page 4, line 39 - page 5, line 9; claim 1 --- -/-	1,11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *G* document member of the same patent family

Date of the actual completion of the international search

28 July 2003

Date of mailing of the international search report

05/08/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Deurinck, P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/SA 02/00086

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 498 596 A (ASHJIAN HENRY ET AL) 12 March 1996 (1996-03-12) column 3, line 26 -column 4, line 28; claims 18,19 -----	17-20, 32-35, 38,39, 46-54, 59,60
X	US 5 569 642 A (LIN KAUNG-FAR) 29 October 1996 (1996-10-29) claims 1,2; example 1; table 2 -----	17-20, 32-39, 46-54, 59,60 1,12-14
A	GB 2 166 782 A (MOBIL OIL CORP) 14 May 1986 (1986-05-14) the whole document -----	1-60

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/02/00086

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6096690	A	01-08-2000	US 6455474 B1 AU 2586497 A WO 9734963 A1	24-09-2002 10-10-1997 25-09-1997
GB 2117429	A	12-10-1983	AU 1166583 A DK 69083 A FR 2521584 A1 WO 8302951 A1 NL 8300608 A AU 1166483 A AU 1166683 A DK 68983 A DK 69183 A FR 2521582 A1 FR 2521583 A1 WO 8302949 A1 WO 8302950 A1 GB 2115458 A GB 2115459 A NL 8300607 A NL 8300609 A NO 830555 A NO 830556 A NO 830557 A	25-08-1983 19-08-1983 19-08-1983 01-09-1983 16-09-1983 25-08-1983 25-08-1983 19-08-1983 19-08-1983 19-08-1983 19-08-1983 01-09-1983 01-09-1983 07-09-1983 07-09-1983 16-09-1983 16-09-1983 19-08-1983 19-08-1983 19-08-1983
US 5498596	A	12-03-1996	AU 1664095 A CA 2172965 A1 EP 0690899 A1 JP 9503017 T NO 951553 A WO 9509215 A1	18-04-1995 06-04-1995 10-01-1996 25-03-1997 24-04-1995 06-04-1995
US 5569642	A	29-10-1996	NONE	
GB 2166782	A	14-05-1986	NO 854412 A	09-05-1986

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (157)